# Determination of As and Se by AAS Using High Intensity Hollow Cathode Lamps

Application Note

Atomic Absorption


## Authors

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## Introduction

The detection of ultra traces of arsenic and selenium in biological samples is very important today. Of special significance is the detection of arsenic and selenium in body fluids. The increasing utilization of gallium-arsenide and selenium dioxide in the semiconductor industry requires regular medical control of As and Se contents in human body fluids. They can be detected in the blood, kidneys, in the skin and in the central nervous system. Selenium plays a dominant role in Vitamin-E metabolism and is of importance for vision. The toxic level lies just over the essential level, so a correct determination for example in blood, is of great importance [1]. Both elements are also measured in environmental samples, for example, in soil, plants and effluents. Arsenic is a by-product in the roasting of sulfide ores and is therefore often determined in the vicinity of typical emission sources such as copper mines.

Selenium plays an important role in animal nutrition, and is an essential element for animal organisms. A selenium deficiency leads to muscle dystrophy (for example, white muscle disease); excessively high selenium concentrations can result in deformed hooves, and a variety of other veterinary illnesses [1].

The fact that the resonance lines of arsenic at 193.7 nm and 197.2 nm lie close to the vacuum UV region means that the normal hollow cathode lamp intensities are often not sufficient. This also applies to selenium, whose most sensitive line is at 196.0 nm. This work compares the normal hollow cathode lamps and the high intensity (Super lamp).

Arsenic and selenium can be determined with the very sensitive hydride technique [2]. However, determinations with the hydride technique do require a pre-reduction of the samples, in order to ensure that the elements are in the correct oxidation state. To avoid chemical pretreatment, these element analyses are often carried out with the graphite furnace AAS (GFAAS), where the dissolved sample can be measured directly. The GFAAS is however not as sensitive as the hydride technique, so that the utilization of the specially intense hollow cathode lamps (Super lamps) for improved sensitivities becomes important.


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## Experimental

### Instrumental

An Agilent SpectrAA-400Z Zeeman graphite tube atomizer was used with Agilent hollow cathode lamps. The boosted discharge, Super lamps were from Photron and were used with their own power supply.

The system from Seiff (Unterschleisham) was used for dissolution of the food sample.

### Reagents

Merck reagents were employed. The certified reference material for Se in Serum was supplied by Utak Laboratories Inc, Canyon Country, California, USA.

### Methodology

A study was carried out on As and Se in aqueous standards. The determination of Se in Serum and in a food sample was also carried out.

### Conditions for As Determination

| | |
|---|---|
| Wavelength | 193.7 |
| SBW | 0.2 nm |
| Sample volume | 10 µL |
| Modifier volume | 10 µL |
| Ashing temperature | 1100 °C |
| Atomization temperature | 2600 °C |
| Modifier | 1 g/L Pd plus 1% Ascorbic acid in a 1:1 ratio |

### Conditions for Se Determination in Aqueous Solutions

| | |
|---|---|
| Wavelength | 196.0 |
| SBW | 1.0 nm |
| Sample volume | 10 µL |
| Modifier volume | 10 µL |
| Ashing temperature | 1200 °C |
| Atomization temperature | 2700 °C |
| Modifier | 1 g/L Pd plus 1% Ascorbic acid in a 1:1 ratio |

### Conditions for the Determination of Se in Serum

| | |
|---|---|
| Sample Preparation | Serum 1+4 volumes of a 1% Triton-X-100 solution |

The method of standard addition was employed, utilizing the sampler "automixing" mode. The temperature and sampler program are shown in Tables 1 and 2.

*Table 1. Temperature Program for Se in Serum*

| Step no. | Temperature (°C) | Time (seconds) | Gas flow (L/min) | Read command |
|---|---|---|---|---|
| 1 | 70 | 5.0 | 3 | No |
| 2 | 120 | 30.0 | 3 | No |
| 3 | 120 | 5.0 | 3 | No |
| 4 | 600 | 10.0 | 3 | No |
| 5 | 600 | 5.0 | 3 | No |
| 6 | 1200 | 15.0 | 3 | No |
| 7 | 1200 | 5.0 | 3 | No |
| 8 | 1200 | 2.0 | 0 | No |
| 9 | 2700 | 0.9 | 0 | Yes |
| 10 | 2700 | 2.0 | 0 | Yes |
| 11 | 2700 | 2.0 | 3 | No |

*Table 2. Sampler Program for Se in Serum*

| | Volume (µL) | | | |
|---|---|---|---|---|
| | Standard | Sample | Blank | Modifier |
| Blank | – | – | 15 | 20 |
| Addition 1 | 2 | 5 | 8 | 20 |
| Addition 2 | 4 | 5 | 6 | 20 |
| Sample | – | 5 | 10 | 20 |

### Experimental Conditions for the Determination of Se in Foodstuffs [5]

Dissolution procedure: 500 mg of homogenized, dried sample material were treated with $HNO_3$ in a closed system (Seiff). The two vessels were combined and made up to 20 mL with pure water. The analysis of cabbage is shown here as an example of the procedure.

## Discussion

### Design and Operation of Hollow Cathode Lamps (HCL)

A hollow cathode lamp [3] consists of a rare (neon or argon) gas filled glass cylinder into which are included one cathode and one anode. The cathode is in the form of a hollow cylinder and either contains or is coated with the element to be determined. The anode can have different forms, such as a wire or rod. A potential is applied between these electrodes, whereby the discharge is initiated and maintained. The anode material is typically made from zirconium or tungsten. When a high potential is applied to these electrodes, the cathode material is bombarded by positively charged gas atoms. The hollow cathode material atoms are excited via further collisions and then emit their characteristic spectrum when they fall back to their ground state. An increase in the applied lamp current leads to a positive effect on the emitted signal to noise ratio. However a negative aspect is the associated broadening of the resonance line, and can even result in so-called self-absorption. These effects lead to a reduction in the absorption sensitivity and a reduction in the lifetime of the lamps.

### Design and Operation of Boosted Discharge Super Lamps (SL)

The boosted discharge Photron lamp [4] is an improved version of the traditional hollow cathode lamp. It has an additional cathode which functions as an electron source. These extra electrons excite the remaining ground state atoms and thus minimize self-absorption. As a result, the Super lamp can operate with a higher lamp current and produce a markedly higher intensity emission spectrum. The intensity of the resonance line in the Super lamp is about 5–10 times higher than in the normal hollow cathode lamp. Figure 1 shows the arsenic emission lines at 193.7 nm for both a hollow cathode lamp and Super lamp. The higher intensity line leads to an increase in sensitivity, an improvement in the signal to noise ratio, and a more linear calibration curve. The optimization of the Super lamp is straight forward, although an additional power supply is required. It is necessary to select a boost current as well as the normal lamp current.

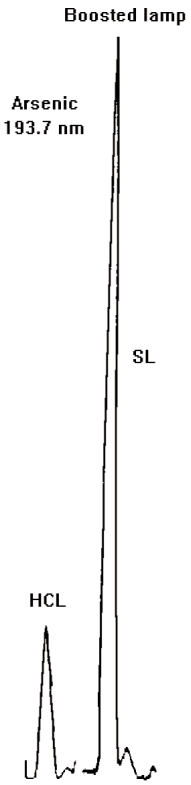


*Figure 1. Emission lines for As at 193.7 nm for both hollow cathode lamp and Super lamp.*

## Results

In measurements with a Super lamp it is difficult to utilize deuterium background correction because intensity of the Super lamp is so high that it is extremely difficult to balance it with the $D_2$ lamp emission intensity. Figure 2 shows signal graphics for As signals from two different concentrations obtained with a HCL. Figure 3 shows the same two measurements with the Super lamp. In Figure 4 are shown the two Se calibration graphs obtained with HCL and Super lamps.

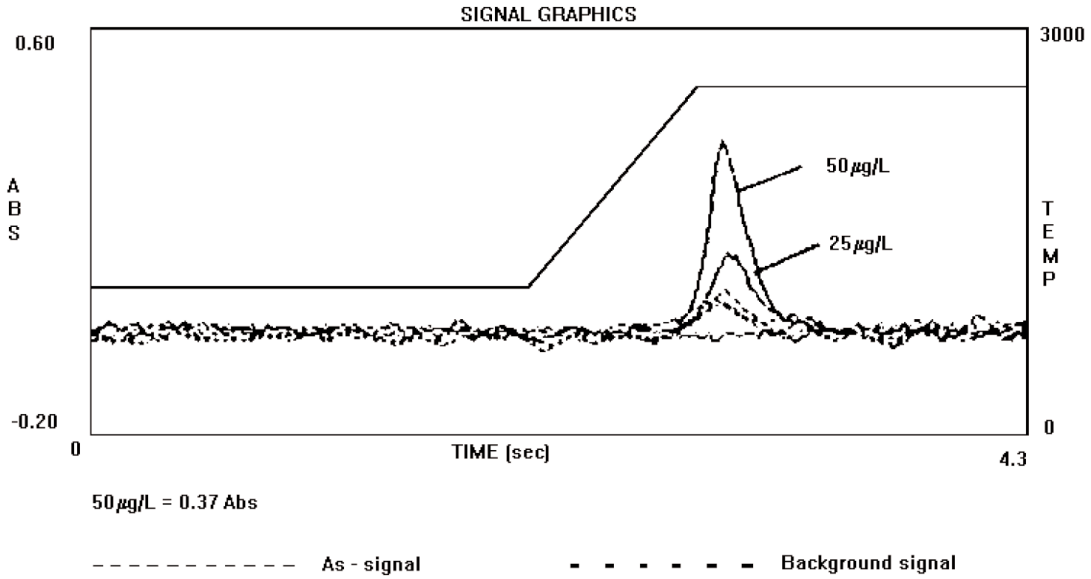


*Figure 2. As signal for standards (HC lamp).*

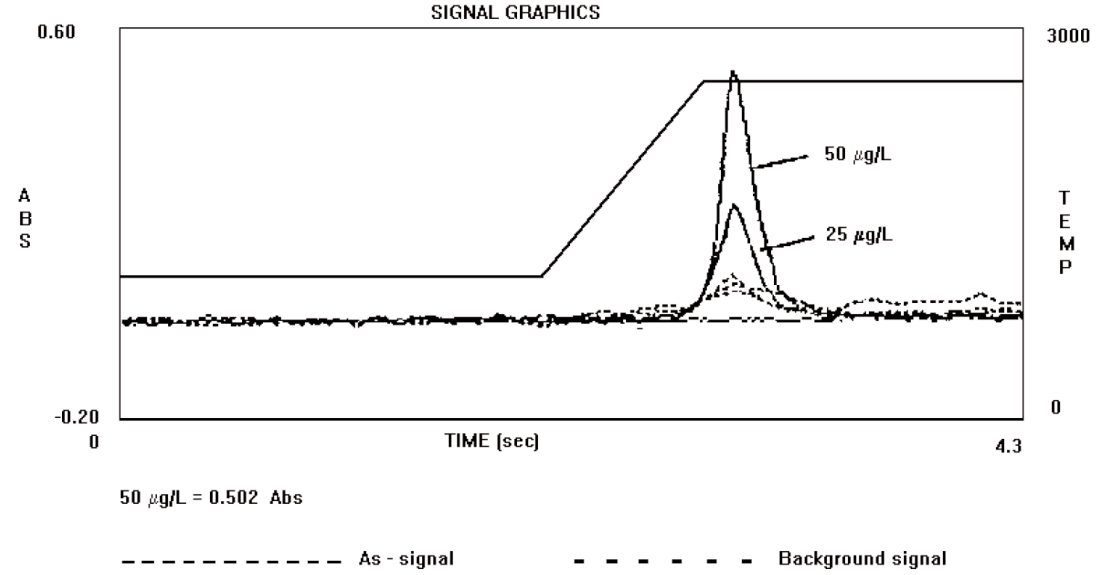


*Figure 3. As signal for standards (Boosted lamp).*

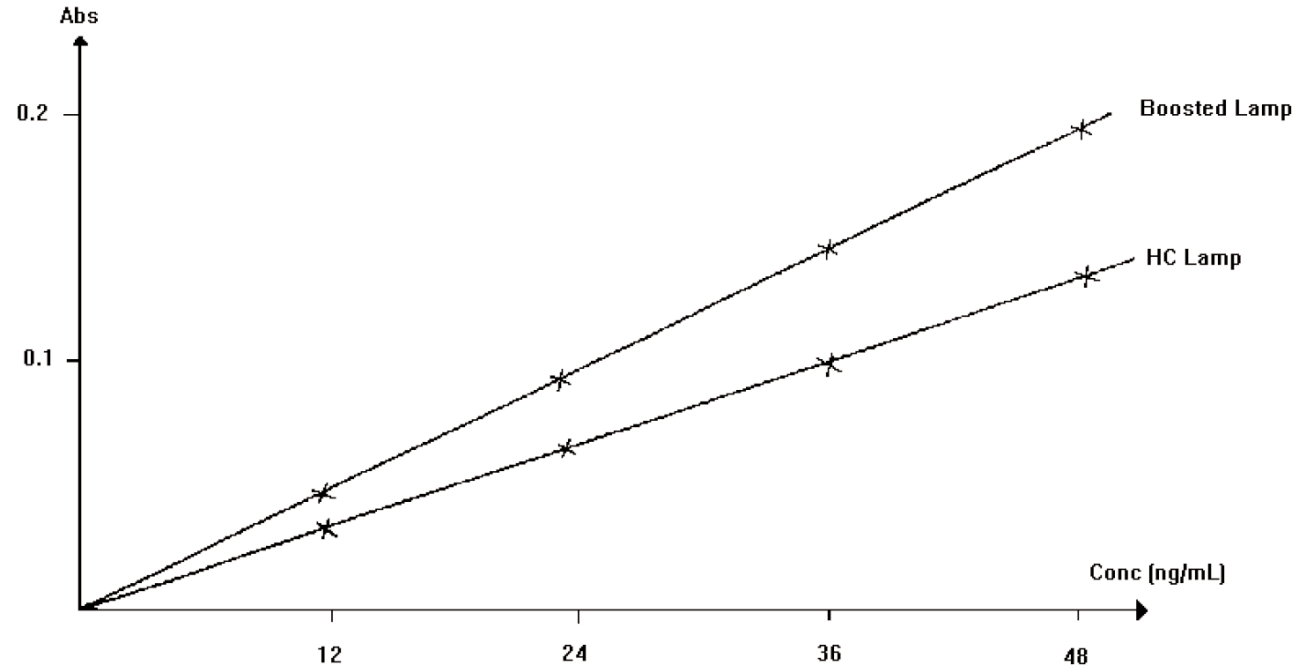


*Figure 4. Normal calibrations for Se (HCL and SL).*

Tables 3 and 4 show the temperature and sampler program for the determination of selenium in food. Both standard addition graphs for the food analysis are shown in Figure 5.

*Table 3. Temperature Program for Measurement of Se in Cabbage*

| Step no. | Temperature (°C) | Time (seconds) | Gas flow (L/min) | Read command |
|---|---|---|---|---|
| 1 | 85 | 10.0 | 3 | No |
| 2 | 95 | 30.0 | 3 | No |
| 3 | 120 | 20.0 | 3 | No |
| 4 | 300 | 10.0 | 3 | No |
| 5 | 1300 | 15.0 | 3 | No |
| 6 | 1300 | 10.0 | 3 | No |
| 7 | 1300 | 2.0 | 0 | No |
| 8 | 2600 | 0.7 | 0 | Yes |
| 9 | 2600 | 1.5 | 0 | Yes |
| 10 | 2700 | 1.5 | 3 | No |

*Table 4. Sampler Program for Measurement of Se in Cabbage*

| | Volume (µL) | | |
|---|---|---|---|
| | Solution | Blank | Modifier |
| Blank | – | 10 | 10 |
| Sample | 10 | – | 10 |

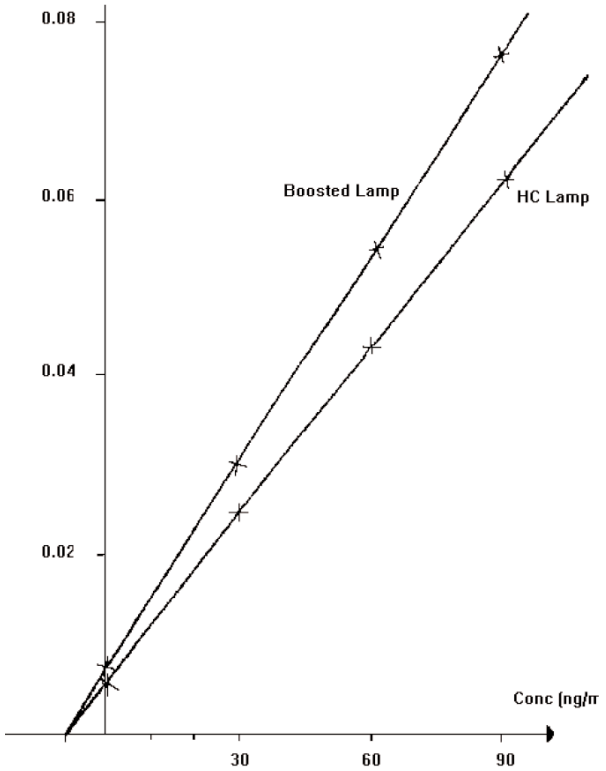


*Figure 5. Standard additions calibration for Se in a food sample for both hollow cathode lamp and Super lamp.*

For the determination of As and Se in aqueous solution an improvement in sensitivity of about 30–40% can be achieved by the use of a high intensity hollow cathode lamp. Thus, 10 µL solution of 50 µg/L As gave 0.502 absorbance with the Super lamp whereas only 0.370 absorbance was obtained with a normal hollow cathode lamp. The results from the determinations of Se in serum and in the sample of cabbage are given in Table 5. In this case also, the use of a Super lamp gives increased sensitivity.

*Table 5. Results for Se in Serum and Cabbage (µg/g)*

| Lamp type | Serum | Cabbage |
|---|---|---|
| HCL | 0.36 | 0.22 |
| SL | 0.35 | 0.18 |

The determination of Se in serum in a certified reference material (Utak Laboratories, Inc.) was also carried out. Certified: 0.387 µg/g, Range of confidence: 0.345 to 0.425 µg/g.

The given range of confidence for Se concentration was obtained with both the hollow cathode lamp and the Super lamp. The utilization of super lamps for aqueous standards and samples with high matrix content results in improved sensitivities.

## References


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